STERIC EFFECTS ON TWO METHYL INTERNAL ROTATIONS OF 2,6- AND 3,4-DIMETHYLFLUOROBENZENE

SAFA KHEMISSI, JULIE MELAN, HA VINH LAM NGUYEN, *CNRS UMR 7583, Université Paris-Est Créteil, Université de Paris, Laboratoire Interuniversitaire des Systèmes Atmosphériques (LISA), Créteil, France*.

The microwave spectra of two dimethylfluorobenzene isomers, 2,6- and 3,4-, were measured using two pulsed molecular jet Fourier transform microwave spectrometers operating in the frequency range from 2.0 to 40.0 GHz with the goal of quantifying the steric effects on the barriers to internal rotation of the two methyl groups. Due to the internal rotations of two equivalent methyl groups in 2,6-dimethylfluorobenzene[a] (26DMFB), all rotational transitions split into quartets, while quintets appear for 3,4-dimethylfluorobenzene[b] (34DMFB) because its two methyl groups are inequivalent. The splittings were analyzed and modeled to deduce a torsional barrier of 236.7922(21) cm^{-1} for the two methyl groups in 26DMFB and of 456.20(13) cm^{-1} and 489.78(15) cm^{-1} for the methyl groups at the *meta* and *para* positions, respectively, in 34DMFB. Each torsional species was fitted separately using odd power order parameters to check the correctness of the assignment. For both isomers, a global fit obtained with the program *XIAM*[c] has achieved a standard deviation close to the measurement accuracy. The experimental results are compared with the predicted values obtained by quantum chemical calculations and those of other toluene derivatives.

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[a] S. Khemissi, H.V.L. Nguyen, ChemPhysChem 2020, 21, 1682-1687.

[b] J. Mélan, S. Khemissi, H.V.L. Nguyen, Spectro. Chem. Acta A 2021, 253, 119564.

[c] H. Hartwig, H. Dreizler, Z. Naturforsch. 1996, 51a, 923-932.